# CLAY STABILIZATION IN SUB-SURFACE FORMATIONS

## FIELD OF THE INVENTION

The present invention generally relates to compositions and methods of using same for clay stabilization in sub-surface formations. More specifically, the present invention relates to compositions that include a polymer that is capable of inhibiting clay swelling and methods of using same for clay stabilization, such as in oil and gas well treatment.

## BACKGROUND OF THE INVENTION

Hydraulic fracturing has been utilized for many years to stimulate the production of oil, gas or other formation fluids from subterranean formations. In hydraulic fracturing, a suitable fluid is introduced into the down-hole formation by way of a well bore under conditions of flow rate and pressure which are at least sufficient to create or extend a fracture into a desired portion of the formation. Various fluids have been utilized in hydraulic fracturing. Most fluids utilized today, however, are aqueous-based liquids.

The presence of clay in oil and gas producing formations poses a problem for production from wells completed in such formations. Ordinarily, such clays are inert in the formation and do not disrupt the flow of hydrocarbons. When disturbed, however, by aqueous-based fluids used in well stimulation for example, clay particles can swell and reduce formation permeability.

Clay swelling problems in the past have been addressed by preflushing with slugs of salt-containing water and using inorganic salts in the aqueous stimulation fluid. Quite often the salt of choice has heretofore been potassium chloride (KCl) which converts the clay to a less swellable form by cationic exchange with $Na^{30}$ ions present on the clay surfaces. Other salts include calcium chloride, ammonium chloride and the like, typically dissolved in an aqueous preflush and/or in the aqueous stimulation fluid used for the formation treatment.

Clays dispersed throughout oil-producing formations may be described as stacked platelets with a net positive charge associated with the four short dimensional sides and a net negative charge

associated with the two long dimensional faces. It is generally believed that the concept of surface charge may be used to understand the mechanisms involved in swelling inhibition. When the large negatively charged face or surface is exposed to an aqueous solution, it attracts cations from the solution. In order to inhibit the swelling phenomenon, minimization of the hydratable surface area of the clay is necessary. One way that this may be accomplished is by flocculating and decreasing the surface charge density, or by increasing the ionic strength of the aqueous phase, or both. By allowing cations with small charge-to-surface-area ratios to associate with the particle, the effective strength of the negatively charged, double-face platelet layer surfaces will be diminished, allowing greater platelet-platelet interaction. Increasing the ionic strength of the solutions will also have the same effect.

In the case of potassium chloride, it is generally believed that the potential for clay swelling is shunted via a cation exchange of potassium ions for the more hydration-enticing native cations, such as sodium. It has been found that K+ is much better at creating electrostatic links between the negatively charged faces of the stacked clay platelets than the abundant Na+, thus allowing less osmotic migration of water to occur between the platelets. While a lower concentration of K+ ions relative to Na+ ions is needed to flocculate clays, $NH_4$+ ions have been shown to be even better or equal to K+ ions in creating electrostatic links and reducing osmotic migration of water.

While salts may be effective in protecting the formation, several problems are generally associated with use of same. For example, the amount of material needed for preparing an effective fluid may be very high, and it is often difficult to dissolve such solid components in the treating fluids in the quantities required. In environmentally sensitive areas, there may be limits on the permissible amount of chloride. The presence of salts may also interact with other additive components of the aqueous stimulation fluid, such as, for example, viscosifying agents, the hydration of which is inhibited by such salts. Further, the duration of the stabilizing effect thereof generally cannot be tailored to meet the optimum duration for a given situation. Accordingly, there is a need for a down-hole clay stabilizing composition that is more inert to other down-hole fluid additives, lower in chloride ion and therefore more environmentally tolerable, which has enhanced clay stabilizing effectiveness compared to potassium chloride and other similar salts, and which may be tailored as to the duration of stabilizing effect.

## SUMMARY OF THE INVENTION

The present invention generally relates to compositions and methods of using same for clay stabilization in sub-surface formations, such as in oil and gas well treatment. The compositions include a polymer, such as a cationic polymer, that is capable of effectively inhibiting clay swelling in a down-hole formation, and can be used to treat and/or pretreat a sub-surface formation for well stimulation, such as fracturing, acid treating and the like. In an embodiment, the present invention provides a composition suitable as an additive for inhibiting clay swelling in a down-hole formation, a well stimulation fluid that includes such composition, and a method for stabilizing a clay-containing formation that employs such compositions as such well stimulation fluids.

The present invention generally relates to compositions that can be effectively utilized to stabilize clays in sub-surface formations. The compositions are added to the sub-surface formations in an effective amount such that clay swelling can be effectively inhibited. In this regard, the present invention can be effectively utilized to treat and/or pretreat a down-hole formation for well stimulation, such as fracturing, acid treating and the like.

In an embodiment, the present invention provides a composition for clay stabilization in a sub-surface formation. The composition comprises one or more polymers selected from the group consisting of poly(dimethylaminoethylmethacrylate quaternary salt), poly(dimethylaminoethylacrylate quaternary salt) and dimethylaminoethylmethacrylate quaternary salt-dimethylaminoethylacrylate quaternary salt copolymer, wherein the polymers have a molecular weight of about 1,000 to about 100,000.

In an embodiment, the polymers have a molecular weight of about 1,000 to about 10,000.

In an embodiment, the polymers are selected from the group consisting of poly(dimethylaminoethylmethacrylate methyl chloride quaternary salt), poly(dimethylaminoethylacrylate dimethylsulfate quaternary salt) and dimethylaminoethylmethacrylate methyl chloride quaternary salt-dimethylaminoethylacrylate methyl chloride quaternary salt copolymer.

In an embodiment, the composition comprises an aqueous solution of poly(dimethylaminoethylmethacrylate methyl chloride quaternary salt).

In an embodiment, the composition further comprises one or more ingredients in addition to the polymer, wherein the ingredients including viscosifying agents, crosslinking agents, bactericides, breakers, ion control agents, foaming agents including a surfactant, a gas stabilizers and liquefied gas stabilizers and combinations thereof.

In an embodiment, the composition is in a form selected from the group consisting of a solution, an emulsion and a powder.

In another embodiment, the present invention provides a stimulation fluid. The stimulation fluid comprises an aqueous solution of one or more polymers selected from the group consisting of poly(dimethylaminoethylmethacrylate quaternary salt), poly(dimethylaminoethylacrylate quaternary salt) and dimethylaminoethylmethacrylate quaternary salt-dimethylaminoethylacrylate quaternary salt copolymer, wherein the polymers have a molecular weight of about 1,000 to about 100,000.

In an embodiment, the stimulation fluid comprises an aqueous solution of poly(dimethylaminoethylmethacrylate methyl chloride quaternary salt).

In an embodiment, the stimulation fluid comprises up to about four gallons of the poly(dimethylaminoethylmethacrylate methyl chloride quaternary salt) solution per 1,000 gallons of stimulation fluid.

In an embodiment, the stimulation fluid of comprises about one to about two gallons of the poly(dimethylaminoethylmethacrylate methyl chloride quaternary salt) solution per 1,000 gallons of stimulation fluid.

In an embodiment, the stimulation fluid further comprises one or more components such as viscosifying agents, crosslinking agents, bactericides, breakers, ion control agents, foaming agents including a surfactant, gas stabilizers and liquefied gas stabilizers, combinations thereof and the like.

In yet another embodiment, the present invention provides a method of stabilizing a clay-containing formation during a sub-surface well stimulation process. The method includes

(i) providing a stimulation fluid comprising an aqueous solution of one or more polymers selected from the group consisting of poly(dimethylaminoethylmethacrylate quaternary salt), poly(dimethylaminoethylacrylate quaternary salt) and dimethylaminoethylmethacrylate quaternary salt-dimethylaminoethylacrylate quaternary salt copolymer, wherein the polymers have a molecular weight of about 1,000 to about 100,000; and

(ii) contacting the sub-surface with the stimulation fluid.

In an embodiment, the stimulation fluid comprises an aqueous solution of poly(dimethylaminoethylmethacrylate methyl chloride quaternary salt).

In an embodiment, the stimulation fluid of comprises up to about four gallons of the poly(dimethylaminoethylmethacrylate methyl chloride quaternary salt) solution per 1,000 gallons of stimulation fluid.

In an embodiment, the stimulation fluid comprises about one to about two gallons of the poly(dimethylaminoethylmethacrylate methyl chloride quaternary salt) solution per 1,000 gallons of stimulation fluid.

In an embodiment, the stimulation fluid further includes one or more components such as viscosifying agents, crosslinking agents, bactericides, breakers, ion control agents, foaming agents including a surfactant, gas stabilizers and liquefied gas stabilizers and combinations thereof.

An advantage of the present invention is to provide improved compositions for clay stabilization.

Another advantage of the present invention is to provide improved clay stabilizers that can be utilized in stimulation fluids.

Yet another advantage of the present invention provides improved compositions that include a low molecular weight polymer for effective clay stabilization without addition of a salt or the like.

Yet still another advantage of the present invention provides improved stimulation fluids and methods of using same to provide clay stabilization in a sub-surface formation.

Additional features and advantages of the present invention are described in and will be apparent from the following Detailed Description of the Presently Preferred Embodiments.

## DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

The present invention generally relates to compositions and methods of using same for clay stabilization in sub-surface formations, such as in oil and gas well treatment. The compositions include a polymer, such as a cationic polymer, that is capable of effectively inhibiting clay swelling in a down-hole formation, and can be used to treat and/or pretreat a sub-surface formation for well stimulation, such as fracturing, acid treating and the like. In an embodiment, the present invention provides a composition suitable as an additive for inhibiting clay swelling in a down-hole formation, a well stimulation fluid that includes such composition, and a method for stabilizing a clay-containing formation that employs such compositions as such well stimulation fluids.

Hydrocarbon producing formations typically contain some amount of clay. When exposed to water based treating fluids, these clays will absorb water, swell and block pore space. This can reduce permeability or swell, break loose and migrate through the formation to later cause damage in another location. Temporary clay stabilizers, such as salts, can be small enough in size to move into the pore throats of the formation matrix, but the effect is only temporary. With respect to high molecular weight polymers, they are physically too large in size to effectively move into the pore spaces of low permeability formations and actually plate out on the formation matrix surface. The present invention provides a composition comprising one or more polymers which are small enough to effectively enter the small pore throats of low permeability formations and further which can provide long term protection.

Further, the present invention can provide less material handling at comparable costs, in comparison to the use of typical inorganic salt treatments. Another general advantage of the present invention concerns the duration of the clay stabilizing effect. At times it is desirable to avoid a stabilization of clay by the use of an organic inhibitor that permanently adheres to the clay particle.

Such adherence may make the clay surface oil wet. An oil wet surface is undesirable when the formation is producing oil to the borehole, since the pressure needed to move oil past an oil wet surface is greater than the pressure needed to move oil past a water wet surface. Therefore, less oil is produced per unit time on an oil wetted surface versus a water wetted surface. The present invention permits the duration of clay stabilization to be tailored to given situations.

In an embodiment, the polymer compositions include polymers prepared by polymerization of the quaternary ammonium salts of dimethylaminoethylmethacrylate, dimethylaminoethyl acrylate and mixtures thereof. The polymers have a molecular weight that is sufficiently low to inhibit clay swelling. For example, the molecular weight can range from about 1,000 to about 100,000, preferably about 1,000 to about 10,000. The composition may, but does not necessarily include a salt, such as KCl, $NH_4Cl$, NaCl, TMAC and the like.

"Quaternary ammonium salts", quaternary salt" and "quat" means the salt resulting from reaction of the tertiary nitrogen atom of dimethylaminoethylmethacrylate, dimethylaminoethyl acrylate with a quaternizing agent or acid. Representative quaternary salts include dimethyl sulfate quaternary salts, benzyl chloride quaternary salts, methyl chloride quaternary salts, and the like. Representative acid salts include hydrochloric acid salt, sulfuric acid salt, and the like.

Preferred polymers include dimethylaminoethylmethacrylate methyl chloride quaternary salt (DMAEM-MCQ), dimethylaminoethylacrylate dimethylsulfate quaternary salt (DMAEA-$MSO_4$Q) and dimethylaminoethylmethacrylate-dimethylaminoethyl-acrylate copolymer (DMAEM-DMAEA). A more preferred polymer is dimethylaminoethylmethacrylate methyl chloride quaternary salt, alone or in combination with other suitable polymer materials, ingredients and the like. Additional ingredients can include, for example, viscosifying agents, crosslinking agents, bactericides, breakers, ion control agents, foaming agents including surfactants, gas stabilizers and liquified gas stabilizers, combinations thereof and the like. In an embodiment, the dimethylaminoethylmethacrylate methyl chloride quaternary salt composition is in an aqueous solution form. However, it should be appreciated that the composition of the present invention can include a solution, an emulsion, a powder and the like.

As previously discussed, the present invention relates to a stimulation fluid that includes a polymer composition in solution form as discussed above. The polymer composition can be added to the stimulation fluid in any suitable concentration. In an embodiment, the stimulation fluid comprises an polymer solution at a concentration of about four gallons of the aqueous polymer composition in solution per 1,000 gallons of stimulation fluid or less, preferably from about one gallon of the aqueous polymer composition in solution per 1,000 gallons of stimulation fluid to about two gallons of the aqueous polymer composition in solution per 1,000 gallons of stimulation fluid. The polymer composition includes at least one of the polymers of this invention, preferably dimethylaminoethylmeth-acrylate methyl chloride quaternary salt, alone or in addition to other ingredients including additional other polyelectrolytes, copolymers thereof, and the like. In an embodiment, the stimulation fluid does not include a salt or other similar type of clay swelling inhibition agent.

The stimulation fluid can be made in any suitable manner. In an embodiment, the stimulation fluid is preferably prepared by admixing a quantity of the clay stabilizing composition of the present invention and a polymeric viscosifying agent with an aqueous fluid. Alternatively, the stimulation fluid may be prepared by blending together the various components, such as the cationic polyelectrolyte and the viscosifier, in the desired proportion in any combination or order.

In an embodiment, the viscosifying agent includes a soluble polysaccharide. Representative examples pf soluble polysaccharides include galactomannan gums (guar), glucomannan gums, cellulose derivatives, and the like. In an embodiment, the stimulation fluid includes a viscosifying agent in a concentration of about 100 to about 600 pounds per 1,000 gallons of the aqueous stimulation fluid.

The stimulation fluid can carry conventional suspended proppants, such as glass beads, which are forced into the fracture or fractures to keep the broken formation from closing completely once the pressure is released. However, the use of such proppants is not necessary to achieve the clay stabilization obtained by the present simulation fluid.

The stimulation fluid also can include a crosslinking agent for the viscosifying agent as well as other suitable additives. For example, the fluid can contain bactericides, breakers, iron control

agents, foaming agents such as surfactants, gases or liquefied gases stabilizers, and the like. The preparation of such fluids and the various additives are well known in the art. The selection of the particular stimulating fluid constituents and amounts thereof such as the viscosifying agent, crosslinking agent, breakers, stabilizers can be made in any suitable manner.

The clay swelling inhibitor composition, or components thereof, are admixed with an aqueous stimulation fluid in an amount sufficient to substantially stabilize the formation against permeability damage as the result of contact with the aqueous stimulation fluid. In this regard, the clay swelling inhibitor composition can be made in a liquid state, in contradistinction to potassium chloride and similar salts which are crystalline solids, and the present composition may be readily admixed with the stimulation fluid at any time prior to contact of the fluid with the formation. Alternatively, the present composition may be admixed with constituents of the liquid viscosifying agent and stored as a ready-to-use stimulation fluid additive concentrate.

The clay swelling inhibitor additive is effective in treating a down hole formation when transported in a carrier fluid, such as a well-stimulation fluid having either an acid, alkaline or neutral pH. The stimulation fluid of the present invention can have a pH in the range of from about 0 to about 11 without any significant negative effects upon the activity thereof, although preferably the pH of the stimulation fluid is within the more moderate range of from about a pH of 0 to about a pH of 10 according to an embodiment of the present invention.

It should be appreciated that the present invention can be made and used in any suitable manner, can include any suitable materials and be modified in any suitable manner. Examples of various and suitable materials, such as stimulation fluid additives, of the present invention can be found in U.S. Patent Nos. 5,342,530; 5,152,906; and 5,099,923, the disclosures of which are herein incorporated by reference.

An illustrative example of the present invention according to an embodiment is provided below without limitation.

Table I: Synthesis of Polydimethylaminoethylmethacrylate-methyl chloride quaternary salt Solution (DMAEM-MCQ Solution)

| Step # | DMAEM-MCQ Solution | grams (g) | Wt% in Formulation |
|---|---|---|---|
| 1 | Dimethylaminoethylmethacrylate methyl chloride quaternary salt (75wt% aq) (DMAEM-MCQ) | 316.8 | 31.68 |
| 2 | D.I. Water | 318.92 | 31.89 |
| 3 | Sodium Hypophosphite hydrate (solid) | 3.56 | 0.356 |
| 4 | Vazo 67 | 0.64 | 0.064 |
| 5 | Methanol | 193 | 19.3 |
| 6 | D.I. Water | 167.08 | 16.71 |
| 7 | Total grams | 1,000 | 100.0 |

A DMAEM-MCQ Solution was made according to an embodiment of the present invention as shown in Table I above and further described in detail below. To a 2-liter 4-neck round bottom flask equipped with an overhead stirrer, a nitrogen ($N_2$) inlet tube, a Dean-Stark trap, an overhead condenser, and a temperature regulator probe installed was added DMAEM-MCQ, water, and sodium hypophosphite with stirring (Material steps 1-3, amounts described above). Stirring of the materials was conducted at room temp, an $N_2$ purge was started at 500 milliliters/minute for 30 minutes, and the material mix was heated to 70°C. Vazo 67 was then added to the mixture, stirring was continued, and the $N_2$ purge tube was raised just above the surface of the liquid in the flask (to reduce entrained vapor loss). Within approximately 20 minutes, an exotherm was noted to 74°C. The temperature decreased to 70°C and stirring was continued for approximately 8 hours.

A mass balance was then run on the product (clear, syrup). Approximately 8 grams of material was lost to vaporization. This was assumed to be D.I. water and thus 8 grams of D.I. water was added to the flask and contents stirred. At this point the product was clear, but many bubbles were entrained. Steps 5 and 6 were then conducted where methanol and a final water addition were carried out (see Table I above). Addition of these materials was performed very slowly with stirring. The product appeared hazy for a brief period and then cleared up. The viscosity, specific gravity and

pH were measured for the DMAEM-MCQ Solution made according to an embodiment of the present invention as described above. The following Table II provides the viscosity, specific gravity, and pH data as measured:

Table II

| Material | pH | Spec gravity @ 20°C | Viscosity (cps) LV Spindle 1, 30rpm |
|---|---|---|---|
| DMAEM-MCQ Solution | 4.42 | 1.0552 | 85.4cps (42.7 dial, 2x factor) |

A number of experiments have been conducted that demonstrate the beneficial effects of the present invention. The experiments and results thereof are described below according to an embodiment of the present invention without limitation.

The experiments were conducted to compare the clay stabilization properties of a composition made pursuant to an embodiment of the present invention to commercially available clay stabilization products. As indicated in Table III below, three products were evaluated during this study, namely Products A-C. Product A is a polyepichlorohydrin-trimethylamine quaternary salt that has a molecular weight of about 1,000. This product is commercially available. Product B is a commercially available DMAEMA-methylsulfate quaternary salt that has a molecular weight of about 800,000. Product C is a clay stabilization composition made pursuant to an embodiment of the present invention. More specifically, Product C includes a dimethylaminoethylmethacrylate methyl chloride quaternary salt that has a molecular weight of about 4,000.

The clay stabilization properties of each of Products A-C were evaluated by measuring the permeability in millidarcies (md) of a Bandera Sandstone core after being treated by a standard 3.5% sodium chloride brine to establish a baseline for the test. The permeability was measured initially or before addition of the product clay stabilizer. The permeability was then again measured after the core had been treated with a product clay stabilizer and then flushed with ten pore volumes of deionized (D.I.) water. Each of the product stabilizers were added at various dosage levels measured

in "gpt" where one gpt represents one gallon of product clay stabilizer added to 1,000 gallons of treatment or carrier fluid.

Any decrease in permeability between the before and after measurements indicates that clay swelling has occurred. As shown in Table III below, the product clay stabilizer according to an embodiment of the present invention outperformed product clay stabilizers that are commercially available.

Table III Clay Stabilizer Test

| Product # | Permeability Before (md) | Dosage (gpt) | Permeability After (md) |
|---|---|---|---|
| A | 4.2 | 1 | 0.5 |
| A | 3.2 | 10 | 3.3 |
| B | 58 | 5 | 46 |
| B | 2.8 | 1 | 1.6 |
| C | 65 | 2 | 68 |
| C | 4.0 | 2 | 3.8 |
| C | 2.6 | 1 | 1.7 |

It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the present invention and without diminishing its attendant advantages. It is therefore intended that such changes and modifications be covered by the appended claims.